

Evaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 1, Dispersant Effectiveness as a Function of Energy Dissipation Rate

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Received: November 24, 2008

Accepted in revised form: February 19, 2009

Abstract

Numerous laboratory test systems have been developed for the comparison of efficacy between various chemical oil dispersant formulations. However, for the assessment of chemical dispersant effectiveness under realistic sea state, test protocols are required to produce hydrodynamic conditions close to the mixing, transport, and dilution effects found in the natural environment. To this end, we have designed and constructed an experimental wave tank system capable of generating waves of different energy levels, ranging from regular non-breaking waves to plunging breakers. The hydrodynamics of these wave conditions were characterized using an autocorrelation function method applied to *in situ* velocity measurements. We report here an investigation of the effectiveness of two chemical dispersants (Corexit 9500 and SPC 1000) on two crude oils (weathered MESA and fresh ANS) under three different wave conditions in the wave tank operated in batch mode. Corexit 9500 dispersed approximately 75% of the weathered MESA and more than 90% of the fresh ANS crude, and SPC 1000 dispersed about 53 and 64%, respectively. Under control conditions (absence of chemical dispersant), only 10 to 20% of the crude oils were dispersed. Quantitative relationships were established between dispersant effectiveness and energy dissipation rate under the different simulated wave conditions. These relationships are essential for the development of accurate predictive models on dispersant effectiveness and operational guidelines for dispersant use.

Key words: oil spill; dispersant effectiveness; energy dissipation rate; breaking waves

Introduction

NATURAL PHYSICAL DISPERSION of oil spills through wave action results in the formation of oil-in-water emulsions of μm -scale oil droplets (Delvigne and Sweeney, 1988; Lee *et al.*, 2001; Daling *et al.*, 2003). The application of chemical dispersants accelerates dispersion of oil by reducing the oil-water interfacial tension, which facilitates droplet formation and results in reduced droplet collision rates as the oil is diluted in the water column (Lessard and Demarco, 2000; NRC, 2005; Chapman *et al.*, 2007). In addition, chemical dispersants promote the formation of smaller droplets than those generated solely by physical dispersion, and can also change the surface thermodynamic properties of the oil to increase the stability of these small oil droplets in seawater. The effec-

tiveness of chemical dispersants depends on hydrodynamic conditions, chemical properties of both dispersant and oil, and a variety of environmental factors (NRC, 1989, 2005; Fingas, 2000).

The importance of wave action for physical and chemical dispersion of oil has been recognized (Delvigne and Sweeney, 1988; Li and Garrett, 1998; Tkalich and Chan, 2002; Shaw, 2003). Oil dispersion effectiveness is determined by several related processes, including initial breakup of the oil slick into small oil droplets, transport and dilution of oil droplets in the water column, and coalescence and resurfacing of oil droplets. The formation of droplets occurs during oil breakup under the influence of mixing energy as the turbulent structure of breaking waves stretch and split the oil by velocity shear. The transport and dilution of oil droplets is then regulated by turbulent diffusion and wave propagation. Coalescence and resurfacing of oil is more likely to occur when the dispersed phase volumetric fraction (concentration) is high. Droplet coalescence kinetics are dependent on collision frequency (proportional to the shear and differential surfacing/settling velocity) and collision efficiency, which is determined by

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droplet surface thermodynamic properties. The resurfacing of oil is driven by the buoyancy force that is proportional to surface area or the square of droplet size.

Tests of chemical dispersant effectiveness (DE) are typically conducted on different scales, ranging from laboratory jar tests to mesoscale wave tank testing and large-scale field trials (NRC, 2005). Bench-scale testing can be useful for comparison of dispersant product effectiveness (Venosa *et al.*, 2002; Sorial *et al.*, 2004) and for investigating the effect of environmental factors such as temperature, salinity, and other variables (Chandrasekar *et al.*, 2005; 2006). However, laboratory tests are inherently limited in simulating real field operational performance due to space constraints that are critical for transport and dilution efficiency. To account for the important interplay between wave-propagation and wave-breaking-induced turbulence, we used the wave tank located at the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia, to allow for evaluation of chemical DE under a variety of simulated wave conditions. This wave tank is capable of generating recurrent breaking waves at the same locations by using the frequency sweep technique (Funke and Mansard, 1979), wherein a low-frequency, fast-moving wave is superimposed onto a high-frequency, slow-moving wave, causing the wave to increase in height until it breaks. In characterizing the hydrodynamics of different wave conditions, since the friction associated with velocity shear causes the dissipation of kinetic energy of the fluid and results in a temporal and spatial variation of the energy dissipation rate per unit mass of water (ϵ , in $W \cdot kg^{-1}$ water), the intensity of microscale turbulence of regular nonbreaking and breaking waves was quantified by computing their energy dissipation rate using an autocorrelation function approach (Kresta and Wood, 1993; Kaku *et al.*, 2006). A previous study on the first version of the wave tank demonstrated the significant effects of breaking waves on chemical DE and dispersed oil droplet size distribution (Li *et al.*, 2008a). The present experimental study has been designed to evaluate the effectiveness of chemical dispersants of different formulations on different crude oils under a variety of wave conditions, and to resolve the effects of breaking wave energy dissipation rate and dispersant application on oil dispersion. The quantitative relationships between DE and energy dissipation rates under varying wave conditions have been sought to establish better operational guidelines of dispersant use and to develop improved predictive models of DE in the field. This is the first of a series of two papers; the second paper focuses on elucidating significant factors determining *in situ* dispersed oil droplet size distribution (Li *et al.*, submitted).

Materials and Methods

Wave tank description

Figure 1 shows a schematic of the wave tank used in this research. It measures 32 m long, 0.6 m wide, and 2 m high, with an average water depth of 1.5 m. Different waves are generated by a computer-controlled flap-type wave maker situated at one end of the tank. The wave maker is linked to an adjustable cam that controls stroke length to alter wave-height characteristics; wave frequency is controlled by the rotation speed of the cam. The wave tank can produce both regular nonbreaking waves and breaking waves, with their mixing energy levels quantified in terms of the energy dissi-

pation rate per unit mass of water (ϵ). An autocorrelation function (Kresta and Wood, 1993; Kaku *et al.*, 2006) applied to time-series velocity measurements obtained by an Acoustic Doppler Velocimeter (SonTec/YSI, Inc. San Diego, CA) was used to evaluate ϵ .

Wave conditions

The hydrodynamic characteristics of three wave conditions were characterized prior to oil dispersion experiments. Regular nonbreaking waves were generated with the flap stroke set at 12 cm to produce a constant frequency wave of 0.80 Hz, a wave length of 2.44 m, and a wave height of about 23 cm. Low-energy spilling breakers were created with an 8.4-cm flap stroke by generating alternating trains of high-frequency waves (0.85 Hz, wave length 2.16 m, wave height 18 cm, and duration 20 s) and low-frequency waves (0.48 Hz, wave length 6.77 m, wave height 6 cm, and duration 5 s). Plunging breaking waves were produced with a 12-cm flap stroke and alternating trains of high-frequency waves (0.85 Hz, wave length 2.16 m, wave height 26 cm, and duration 20 s) and low-frequency waves (0.5 Hz, wave length 6.24 m, wave height 9 cm, and duration 5 s). The characterization of the wave tank hydrodynamics has been reported in detail elsewhere (Wickley-Olsen *et al.*, 2008).

Dispersants

Two commercial chemical dispersants, Corexit 9500 and SPC 1000, were tested. Both dispersants are listed on EPA's National Contingency Plan Product Schedule (<http://www.epa.gov/emergencies/content/ncp/index.htm>). The precise formulas of the dispersants are proprietary. Corexit 9500 is a hydrocarbon-based reformulation of water-based Corexit 9527 and is meant to be used on higher viscosity oils and emulsions. SPC 1000 is a water-based formulation.

Crude oils

Two types of crude oil of varying viscosities were tested: (1) medium sulphurous crude oil (MESA), with API (American Petroleum Institute) gravity of 29.7, and (2) Alaska North Slope (ANS), with API of 29.6. MESA oil was obtained from the Petro-Canada Refinery in Montreal (QB, Canada), and was weathered by sparging with air at a pressure of 18 psi for 130 h, resulting in 13.8% evaporation of the volume of oil to simulate the loss of volatile components at sea shortly after a spill. ANS crude oil was provided by ExxonMobil (Fairfax, VA), and was not weathered to enable the testing of DE under ideal conditions where dispersant is applied immediately after a spill.

Experimental design

The wave tank study was conducted using a three-factor (dispersant, oil, and wave) mixed-level ($2 \times 2 \times 3$) factorial experimental design with triplicate runs for every treatment. These treatments were operated in a randomized block design containing three blocks of 12 experimental units per block. The treatments were randomly assigned to the units in each block, with each treatment appearing exactly once in every block. The advantage of a randomized block design over the completely randomized design in this study was to minimize the bias on the observed DE caused by variations in envi-

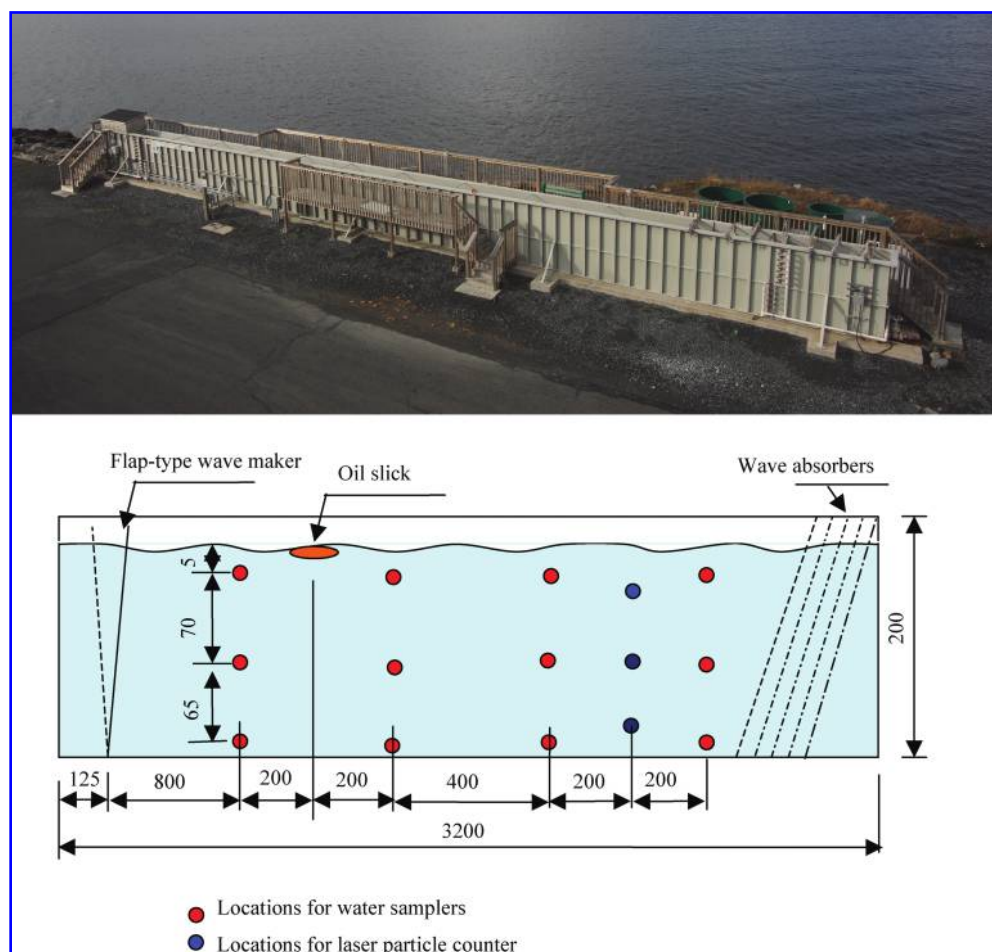


FIG. 1. Photograph (upper) and schematic representation (lower, all dimensions in centimeters, not to scale) of the wave tank facility at the Bedford Institute of Oceanography. Color images available online at www.liebertonline.com/ees.

ronmental conditions such as water temperature, salinity, and wind. Experimental seawater temperature and salinity were recorded as $16.3 \pm 1.8^\circ\text{C}$, and 26.7 ± 3.2 ppt, respectively, during the experimental period.

Experimental procedures

For each experiment, fresh seawater was pumped from the Bedford Basin through a double-layer sock-filter (Atlantic Purification Ltd, Dartmouth, NS, Canada) with a pore size of 25 and 5 μm for the coarse and fine filters, respectively. Background temperature, salinity, and particle size distribution were recorded before each experiment. To start an experiment, 300 mL of crude oil was gently poured onto the water surface within a 40-cm (inner diameter) ring (constructed of NSF-51 reinforced clear PVC tube) located 10 m from the wave maker. Immediately after oil addition, 12 mL of dispersant (or water for the control) was sprayed on top of the oil through a pressurized nozzle (60 psi; 0.635 mm i.d.) resulting in a dispersant-to-oil ratio (DOR) of 1:25. The ring was then lifted immediately prior to the upcoming of the first wave, and waves were generated continually during the next 2 h. Wave tank water samples were collected by using four sets of 100 mL syringes connected to a stainless steel manifold

sampling at four horizontal locations (8, 12, 16, and 20 m downstream from the wave maker), three depths (5, 75, and 140 cm from the average water surface), and four time points (5, 30, 60, and 120 min after initial mixing). Samples were extracted in dichloromethane (DCM) according to EPA Method 3510C (liquid-liquid partitioning) and analyzed for total petroleum hydrocarbons (TPH) with a Genesys 20 ultraviolet spectrophotometer (Thermo Fisher Scientific; Calgary Canada) as described previously (Li *et al.*, 2008a).

DE

DE is defined as the mass of dispersed oil in the water column divided by the total mass of oil added:

$$\text{DE}(\%) = \frac{\bar{C}_{\text{sample}} V_{\text{wt}}}{\rho_{\text{oil}} V_{\text{oil}}} \times 100 \quad (1)$$

where: V_{wt} = total water volume in the wave tank (27,000 L); \bar{C}_{sample} represents the average concentration of oil measured in the water column; ρ_{oil} is the density of the test oil ($\text{g} \cdot \text{L}^{-1}$), and V_{oil} is the volume of oil used in the experiment (300 mL).

The DE of different dispersants on different crude oils can be empirically related by a power law to the energy

dissipation rate, ε , under different wave conditions (Delvigne and Sweeney, 1988; Li *et al.*, 2008a):

$$DE = a \times \varepsilon^b \quad (2)$$

where a and b are dimensionless regression coefficients; ε is energy dissipation rate per unit mass of water in $\text{watt} \cdot \text{kg}^{-1}$ or $\text{m}^2 \cdot \text{s}^{-3}$. Physically, a represents the ultimate maximum DE, and b indicates the dependency of DE on energy dissipation rate for different wave conditions. Equation (2) was applied to perform a nonlinear regression of the experimental observations for different combinations of oil (MESA and ANS) and dispersant (water, Corexit 9500, and SPC 1000). The average DE of the triplicate data was fitted by nonlinear least-squares regression to obtain the kinetic parameters.

Data analysis

The effects of dispersant type, wave type, oil type, and dispersion time on the effectiveness of oil dispersion (as determined by the dispersed oil concentration in the water column) were analyzed using a four-way factorial analysis of variance (ANOVA) using statistical data analysis package S-Plus 7.0 (Insightful Inc., Seattle, WA). When a significant factor was identified, the Tukey's paired comparison method was used to clarify the significance of effect at each treatment level.

Results and Discussion

Hydrodynamic characterization of the three wave conditions

The average energy dissipation rates were estimated to be approximately 0.005, 0.1, and $1 \text{ W} \cdot \text{kg}^{-1}$ near the surface at the mixing zone for regular nonbreaking waves, spilling breaking waves and plunging breaking waves, respectively. The energy dissipation rates declined exponentially to approximately $0.001 \text{ W} \cdot \text{kg}^{-1}$ for the two breaking wave conditions at a depth of 30 cm and decreased linearly under regular nonbreaking wave conditions (Wickley-Olsen *et al.*, 2008). The average energy dissipation rates of the three wave conditions that were investigated in this research are similar to the mixing energies observed in the field. Terray *et al.* (1996) reported ε to vary between 10^{-5} and $10^{-2} \text{ W} \cdot \text{kg}^{-1}$ at a wave height of about 0.25 m in Lake Ontario. Drennan *et al.* (1996) conducted similar measurements in the Atlantic Ocean off the Maryland coast and found ε to vary between $(1 \sim 5) \times 10^{-4} \text{ W} \cdot \text{kg}^{-1}$ at wave heights of 1 m. The high energy dissipation rate under plunging breaking waves in our system was similar to the breaking wave energy dissipation rate reported in the field (Delvigne and Sweeney, 1988; Drennan *et al.*, 1996; Terray *et al.*, 1996), whereas the values for regular waves were similar to those found on the sea surface layer (Delvigne and Sweeney, 1988). Interestingly, the average energy dissipation rates of the three wave conditions measured here are in line with the energy dissipation rates in the Baffled Flask at mixing speed of 100, 150, and 200 rpm, respectively (Kaku *et al.*, 2006). The Baffled Flask has been proposed by the U.S. EPA (Venosa *et al.*, 2002; Sorial *et al.*, 2004) as a replacement of the Swirling Flask Testing (SFT) protocol (EPA, 1996). The SFT was measured to have orders of magnitude lower energy dissipation rates than the

baffled flasks at the standard mixing speed of 150 rpm (Kaku *et al.*, 2006). Disregarding other factors such as transport, dilution, and wall interference, the baffled flasks may provide representative mixing energy levels that are required for the testing of chemical DE in the field.

Effects of dispersant and wave conditions on oil distribution in the wave tank

To evaluate DE, the fraction of added oil entrained in the water column of the wave tank must be determined. This can be accomplished either by measuring the amount of oil remaining on the surface after mixing in the presence of chemical dispersants or by measuring the oil concentration in the water column (NRC, 2005, and refs therein). The indirect method of measuring oil at the surface has been questioned because of incomplete recovery of oil fractions from compartments that cannot be explicitly measured, such as those evaporated into the atmosphere and irreversibly absorbed to the walls (Fingas and Ka'aihue, 2004). In contrast, we collected a large number of samples with high resolution in space and time to directly measure the oil dispersed in the water column. Figures 2 to 4 display representative contour plots of the MESA oil concentration in the wave tank. The ANS oil distributions in the wave tank (data not shown) were similar as those of MESA oil.

Figure 2A shows the control condition where only seawater was sprayed onto the oil slick under regular wave conditions. The added oil, which remained on the surface, was rapidly transported to the end of the tank due to the absence of dispersant that would reduce the oil-water interfacial tension and the lack of sufficient mixing energy to break up the slick. The ineffective natural dispersion of oil under regular wave conditions is clearly shown in Fig. 2A, with high oil concentration on the surface near the wave absorbers, and the slow movement of dispersed oil upstream. In contrast, dispersion of MESA oil was significantly more effective over time after the slick was sprayed with either Corexit 9500 or SPC 1000 (Fig. 2B and C). Although the distribution of oil in the tank was similar to the control at 5 min, the oil became progressively more dispersed over time as its concentration steadily declined at the furthest downstream surface sampling, and the oil plume dispersed upstream and deeper into the water column. The overall dispersion was more evident after the addition of Corexit 9500 (Fig. 2B) than SPC 1000 (Fig. 2C).

Under spilling breaking waves (Fig. 3), the spreading of oil at the surface was enhanced under physical dispersion (Fig. 3A) and chemical dispersion (Fig. 3B and C). This was probably attributable to the dissipation of total kinetic energy as microscale turbulent eddies under the breaking waves, dampening the downstream drift velocity of the water and increasing the turbulent diffusion of dispersed oil droplets. Chemical dispersion by Corexit 9500 (Fig. 3B) or SPC 1000 (Fig. 3C) under spilling breaking waves increased oil dispersion significantly compared to the regular wave conditions (Fig. 2A–C), as indicated by the movement of oil farther upstream. However, the depth of penetration of the oil plume was limited to the upper half of the tank, similar to dispersion under regular wave conditions.

Under plunging breaking waves (Fig. 4A–C), spreading of the oil plume was even more pronounced compared to the

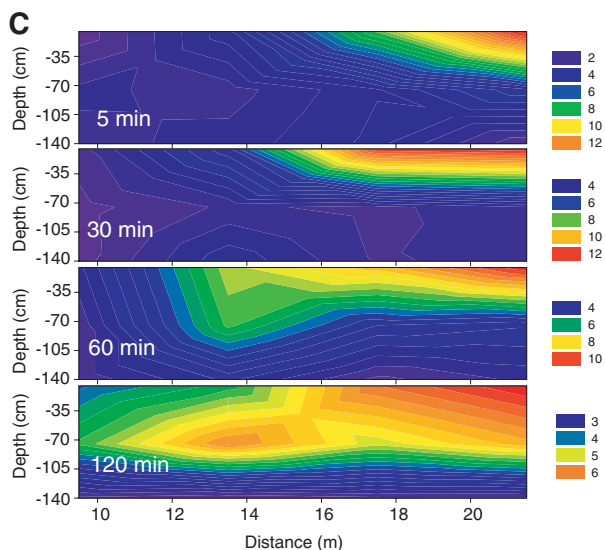
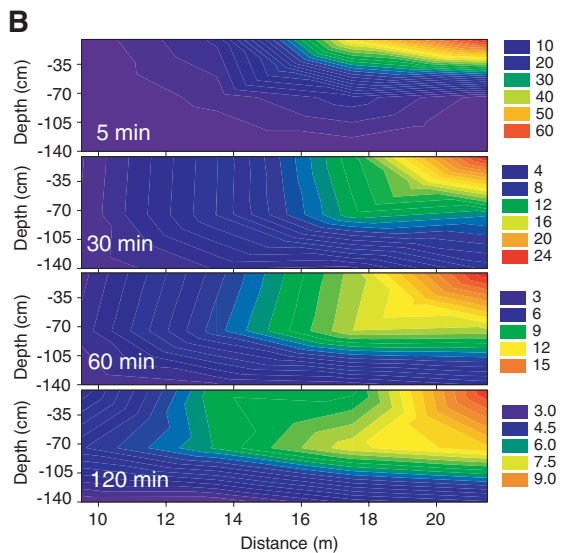
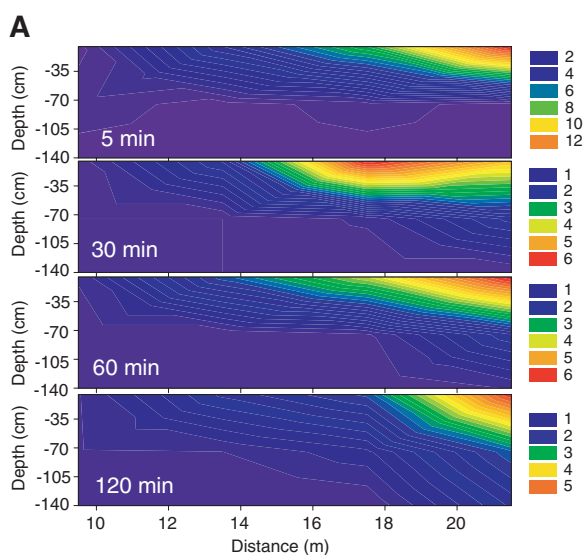
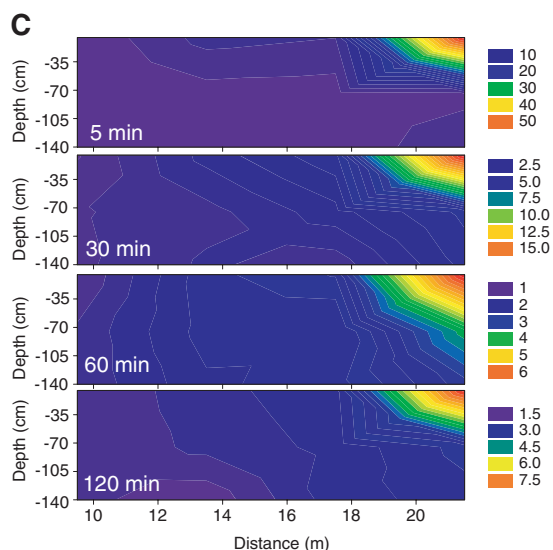
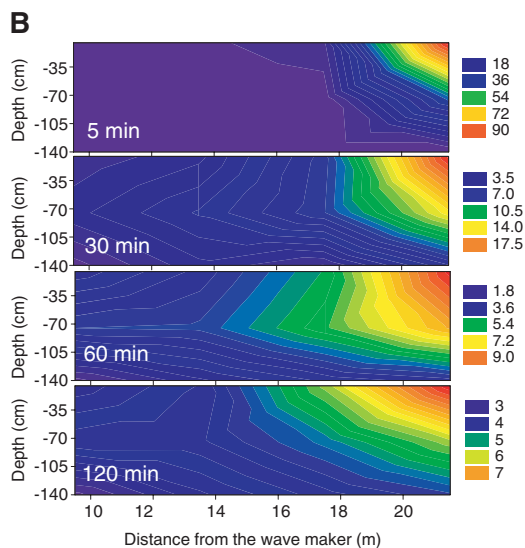
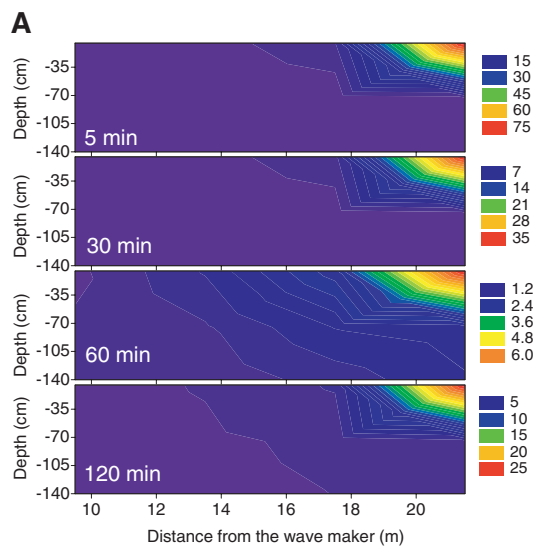


FIG. 2. Dispersed oil concentration ($\text{mg} \cdot \text{L}^{-1}$) as a function of time and space under regular nonbreaking waves: (A) no dispersant; (B) with corexit 9500; (C) with SPC 1000. Color images available online at www.liebertonline.com/ees.

FIG. 3. Dispersed oil concentration ($\text{mg} \cdot \text{L}^{-1}$) as a function of time and space under regular nonbreaking waves: (A) no dispersant; (B) with corexit 9500; (C) with SPC 1000. Color images available online at www.liebertonline.com/ees.

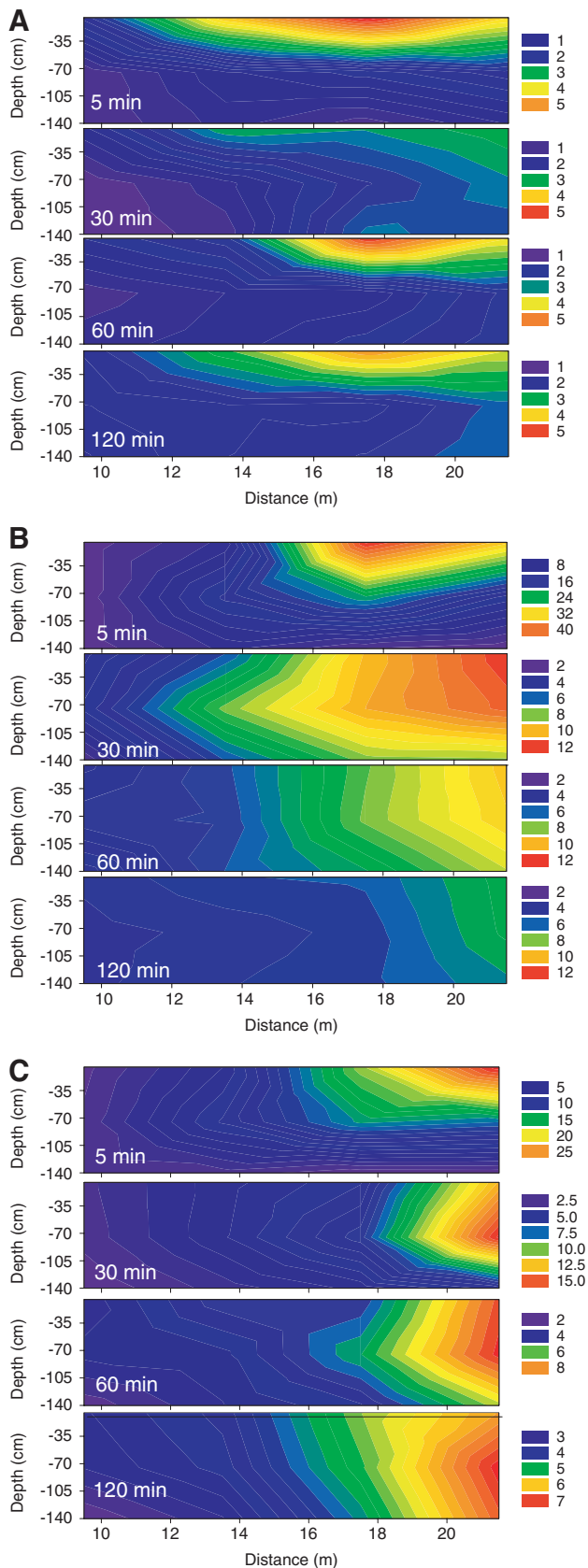


FIG. 4. Dispersed oil concentration ($\text{mg} \cdot \text{L}^{-1}$) as a function of time and space under plunging breaking waves: (A) no dispersant; (B) with corexit 9500; (C) with SPC 1000. Color images available online at www.liebertonline.com/ees.

nonbreaking and spilling breaking waves. In the no-dispersant control condition, spreading at the surface was higher, as shown by the reduced net drifting of oil at the surface (Fig. 4A). In the presence of chemical dispersants, the oil plume appeared virtually homogenized in the wave tank at all depths due to the combined effect of more vigorous turbulent diffusion created by the plunging breaking waves and the presence of chemical dispersants (Fig. 4B and C).

The effect of breaking waves on the oil distribution (in particular, the penetration depth of dispersed oil) is related to a number of contributing factors. As waves break, it is estimated that 30 to 50% of the dissipated wave energy entrains oil droplets into the water column (Lamarre and Melville, 1991; Tkalich and Chan, 2002), and effectively determines the first-order oil entrainment rate (Tkalich and Chan, 2002). Breaking waves develop a mixing layer in the upper water column, and the penetration of oil results in a uniform mixing of the droplets, with the mixing layer proportional to the height of breaking waves (Delvigne and Sweeney, 1988; Tkalich and Chan, 2002). Moreover, breaking waves generate microscale turbulence with the smallest eddies having the greatest velocity gradients, leading to deformation, elongation, and eventual breakup of larger droplets, forming a large number of small droplets that have lower buoyancy and more rapid diffusion efficiency (Delvigne *et al.*, 1987; Li and Garrett, 1998).

DE as a function of energy dissipation rate

DE was determined by estimating the average dispersed oil concentration in the water column for the two chemical dispersant treatments and the no-dispersant (physically dispersed) control as a function of ϵ . This was performed by calculating the average oil concentrations of the eight samples recovered from the four horizontal locations and two lower depths of the water column in the wave tank. It is reasonable to exclude the surface samples from the calculation of the average dispersed oil concentration in the water column because the high oil concentrations on the surface of the water at the wave absorber end of the tank were largely controlled by surface drift, and would skew the calculations of DE. Intuitively, the extremely high oil concentration of the samples recovered from the surface in front of wave absorbers under regular waves in the absence of dispersants is a clear indication of poor oil dispersion efficiency.

Figures 5 and 6 present the estimated DE of the three dispersant types (including water as the control) on the two crude oils as a function of ϵ . Different degrees of physical dispersion of the MESA and ANS crude were measured at each energy dissipation rate. The physical DE of MESA crude ranged from 4 to 9% at 5 min (Fig. 5A), and then steadily increased with time, approaching 12 to 24% after 2 h (Fig. 5D). Similarly, the physical DE of ANS crude was between 3.5 and 9% at 5 min (Fig. 6A) and increased to between 10 and 19% at 2 h (Fig. 6D). Delvigne and Sweeney (1988) have reported that the physical dispersion of oil in a grid column generated droplets that were mostly larger than $50 \mu\text{m}$ in turbulence at energy dissipation rates of up to $3.5 \text{ W} \cdot \text{kg}^{-1}$, but they observed only a very small fraction of oil dispersed by breaking waves under a surface slick in their flume experiments. Lunel (1993, 1995) found that the dispersion of Forties crude oil with and without dispersant applied at sea generated a similar

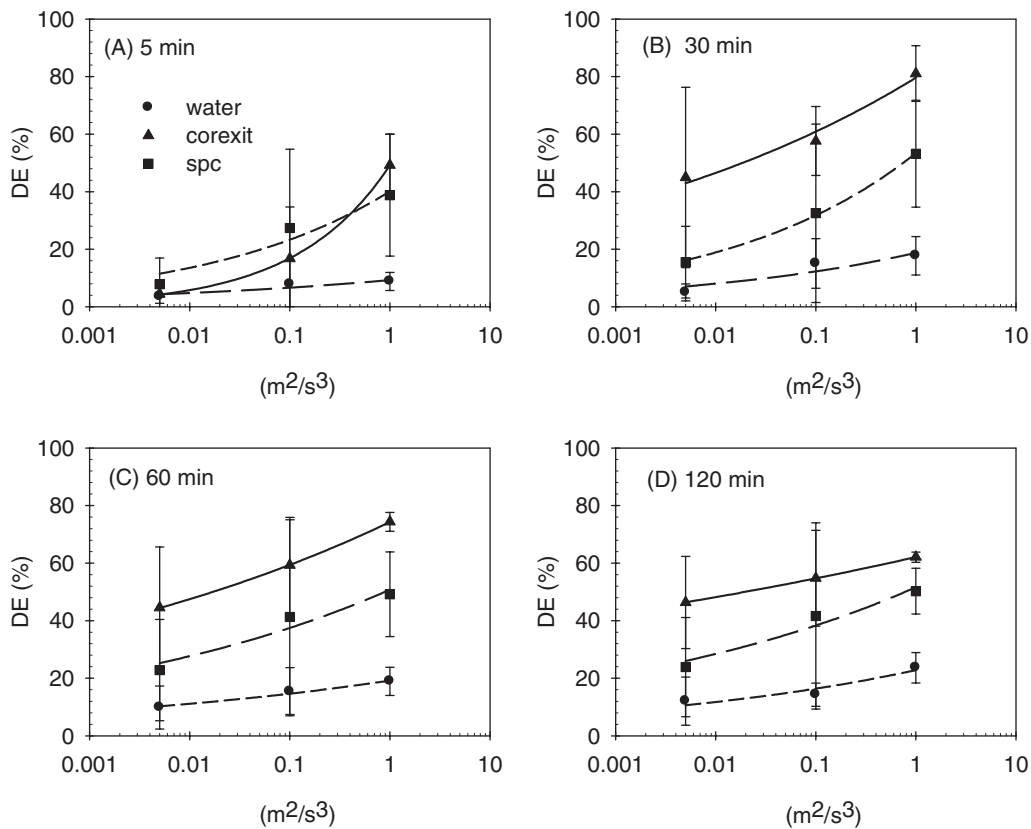


FIG. 5. Dispersant effectiveness (DE) on MESA crude oil as a function of energy dissipation rate at: (A) 5 min, (B) 30 min, (C) 60 min, and (D) 120 min. Data shown are mean and one standard deviation of independent triplicate runs. Lines are best-fit regressions of Equation (2).

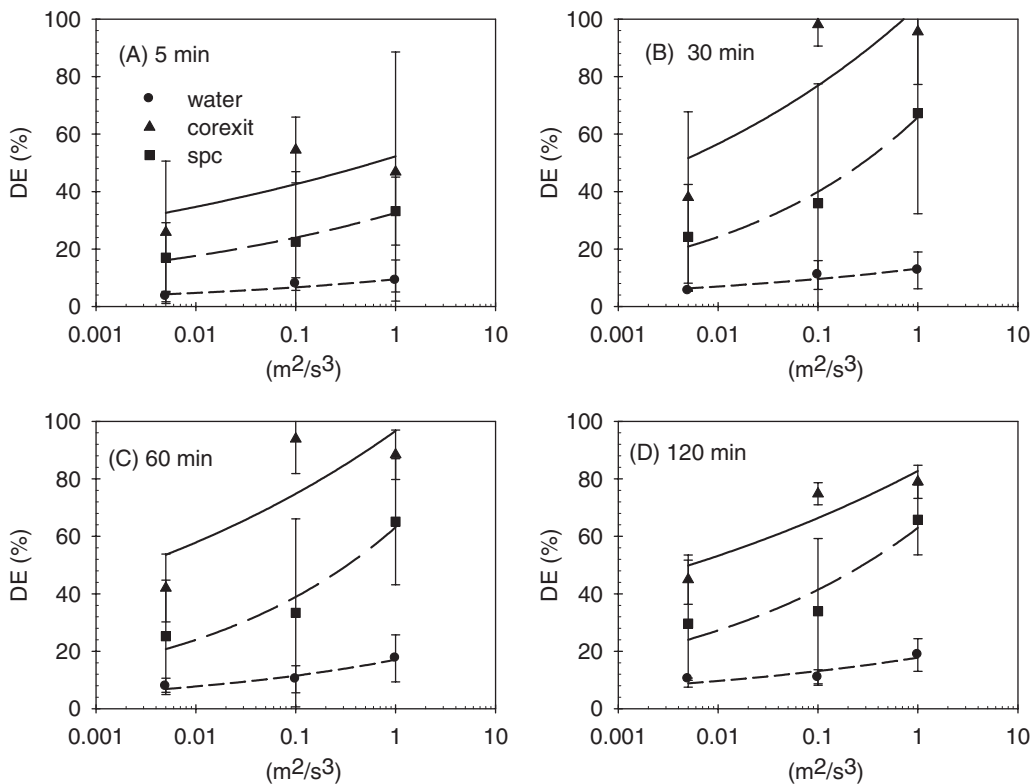


FIG. 6. Dispersant effectiveness (DE) on ANS crude oil as a function of energy dissipation rate at: (A) 5 min, (B) 30 min, (C) 60 min, and (D) 120 min. Data shown are mean and one standard deviation of independent triplicate runs. Lines are best-fit regressions of Equation (2).

TABLE 1. FOUR-WAY FACTORIAL ANALYSIS OF VARIANCE OF THE MAIN FACTOR AND MULTIFACTOR INTERACTION EFFECTS ON THE DISPERSANT EFFECTIVENESS

	Degree of freedom	Sum of square	Mean square	F value	Pr (F)
Dispersant (Disp)	2	627.8180	313.9090	140.2928	0.0000000*
Wave	2	163.0560	81.5280	36.4366	0.0000000*
Time	3	100.6297	33.5432	14.9912	0.0000000*
Oil	1	16.5033	16.5033	7.3757	0.0074208*
Disp/oil	2	19.0702	9.5351	4.2614	0.0159212*
Disp/wave	4	69.9299	17.4825	7.8133	0.0000100*
Oil/wave	2	1.9648	0.9824	0.4391	0.6455039
Disp/time	6	45.2753	7.5459	3.3724	0.0038509*
Oil/time	3	0.4255	0.1418	0.0634	0.9790765
Wave/time	6	7.1573	1.1929	0.5331	0.7824024
Disp/oil/wave	4	28.0072	7.0018	3.1293	0.0167294*
Disp/oil/time	6	1.9656	0.3276	0.1464	0.9895068
Disp/wave/time	12	6.7733	0.5644	0.2523	0.9948054
Oil/wave/time	6	8.4322	1.4054	0.6281	0.7075827
Disp/wave/oil/time	12	5.4511	0.4543	0.2030	0.9981657
Residuals	144	322.2041	2.2375		

*Significant factors.

number of large oil droplets ($>70 \mu\text{m}$), but dispersion of the oil with dispersant produced much greater number of small droplets ($<70 \mu\text{m}$). However, because none of these authors have reported physical DE explicitly, it is impossible to compare their results with our current work, beyond the consistency that physical dispersion of oil was expected. It was even more difficult to obtain physical DE of oil when bench-scale testing apparatus was used, due to coalescence and resurfacing of oil from the relatively large water to oil ratio and the wall effect of confined space (Chandrasekar *et al.* 2005, 2006).

Chemical dispersants were effective under all three wave conditions (Figs. 5 and 6), with oil dispersion most effective under plunging breaking wave conditions and least effective under regular nonbreaking wave conditions. The dispersant Corexit 9500 appeared twice as effective as SPC 1000 for the dispersion of MESA crude at the two lower energy dissipation rates, but the DE of the two dispersants was closer after oil

was dispersed for 2 h at a high-energy dissipation rate. A similar trend was observed for the dispersion of ANS crude. At all three energy dissipation rates, though, the DE of Corexit 9500 was consistently higher than that of SPC 1000, and both were significantly higher than the control. The DE of the control was significantly increased as a function of time at a high-energy dissipation rate. The SPC 1000 was less effective at the two lower energy dissipation rates. In contrast, the Corexit 9500 appeared equally effective at the two higher energy dissipation rates but less effective at the low-energy dissipation rate.

To delineate the effect of each treatment factor on the oil dispersion, a four-way factorial ANOVA was conducted to determine the effects of main factors and multifactor interactions on the DE. The main factors tested included dispersant type (three levels), wave condition (three levels), oil type (two levels), and oil dispersion time (four levels). The oil dispersion time (5, 30, 60, and 120 min) was analyzed sepa-

TABLE 2. TUKEY'S PAIRED COMPARISON OF THE DIFFERENT EFFECTS BETWEEN TREATMENT LEVELS ON DISPERSANT EFFECTIVENESS (%) IN THE WATER COLUMN

Treatment	Level	Estimates	Standard error	Lower limit	Upper limit
Dispersant	Corexit—SPC	21.6*	2.98	14.6	28.7
	Corexit—Water	47.7*	2.98	40.6	54.7
	SPC—Water	26.1*	2.98	19.0	33.0
Wave	Plunging—Regular	24.3*	2.98	17.3	31.4
	Plunging—Spilling	12.3*	2.98	5.5	19.5
	Spilling—Regular	11.8*	2.98	4.7	18.9
Time	30 min—5 min	17.8*	3.29	9.3	26.4
	60 min—5 min	18.5*	3.29	10.0	27.1
	120 min—5 min	17.6*	3.29	9.1	26.2
	60 min—30 min	0.73	3.29	-7.8	9.3
	120 min—30 min	-0.19	3.29	-8.7	8.4
	120 min—60 min	-0.92	3.29	-9.5	7.6

*Significant differences, based on 95% simultaneous confidence intervals for specified linear combinations.

rately to identify the time required to achieve the maximum overall DE for the three dispersant conditions on the two oils under the three imposed wave conditions. The results of the ANOVA are summarized in Table 1. The ANOVA revealed that there was one significant three-factor interaction (dispersant by oil by wave, $p = 0.017$) and three significant two-factor interactions (dispersant by oil, $p = 0.016$; dispersant by wave, $p = 0.00001$; and dispersant by time, $p = 0.00385$). Interactions of these factors indicate that they had opposite effects on the DE. There was no two-way time-by-wave interaction. All four main factors showed very strong significant effects on the DE (oil, $p = 0.0074$; wave, dispersant type, and dispersion time, $p < 0.0000001$).

The Tukey's paired comparison method was used to compare the effects of different levels of the main factors that have been identified to significantly affect the DE; the results are listed in Table 2. The two tested dispersants both have significantly higher DE than the water control (increasing DE by an average margin of 48 and 26%, respectively, for Corexit 9500 and SPC 1000); Corexit 9500 was more effective than SPC 1000 by a 22% higher DE. As for the effect of the wave condition, spilling breaking waves significantly increased DE by 12% compared to the regular nonbreaking waves; plunging breaking waves significantly increased the DE by an additional 13% compared to the spilling breaking waves. With regard to dispersion time, the extent of oil dispersion increased significantly from 5 min to 30 min, and leveled off thereafter.

Conclusion

This study demonstrated the quantitative relationship between chemical DE and energy dissipation rate when the effects of two dispersants on two crude oils were evaluated under three different wave conditions in an experimental wave tank. The mixing energies of these wave conditions were close to those encountered in the field when oil spills are treated with chemical dispersants. The data reported here support the importance of breaking wave conditions in facilitating chemical DE (Nilson *et al.*, 1985; Delvigne and Sweeney, 1988; Tklich and Chan, 2002; Shaw, 2003; Li *et al.*, 2008a). The oil-based dispersant, Corexit 9500, was more effective than the water-soluble dispersant, SPC 1000, in dispersing the two crude oils under all three wave types and energy levels. More studies are needed to evaluate dilution effect on the performance of these dispersants. These results, together with the oil droplet size distribution data (Li *et al.*, 2008b), will have significant implications in developing better operational guidelines for dispersant use and improved predictive models of dispersant effectiveness in the field.

Acknowledgments

This research was funded by the Program of Energy Research and Development (PERD), U.S. EPA (contract No. 68-C-00-159), and NOAA/UNH Coastal Response Research Center (NOAA Grant Number: NA04NOS4190063 UNH Agreement No. 06-085). The authors wish to thank Susan Cobanli, Xiaowei Ma, Brian Robinson, Peter Thamers, and William Yeung for their contributions and logistic support. The findings, opinions, and recommendations expressed in this report are those of the authors and do not necessarily reflect those of the sponsors.

Author Disclosure Statement

The authors declare that no conflicting financial interests exist.

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1. Zhengkai Li , Kenneth Lee , Thomas King , Michel C. Boufadel , Albert D. Venosa . 2009. Evaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 2—Significant Factors Determining In Situ Oil Droplet Size DistributionEvaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 2—Significant Factors Determining In Situ Oil Droplet Size Distribution. *Environmental Engineering Science* **26**:9, 1407-1418. [[Abstract](#)] [[PDF](#)] [[PDF Plus](#)]